

**FINAL REPORT—BERKELEY PIT WATER
TREATMENT RESEARCH PROJECT**

**MINE WASTE TECHNOLOGY PROGRAM
ACTIVITY IV, PROJECT 1**

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Berkeley Pit Water Treatment Research Project Final Report

Foreword

Today, industries are developing and modifying technologies to more efficiently produce their products. The waste generated by these industries, if improperly dealt with, can threaten public health and degrade the environment. The U.S. Environmental Protection Agency (EPA) is charged by Congress with protecting the nation's land, air, and water resources. Under mandate of national environmental laws, the EPA strives to formulate and implement actions leading to a balance between human activities and the ability of natural systems to support and nurture life. These laws direct the EPA to perform research to define, measure the impacts, and search for solutions to environmental problems.

The National Risk Management Research Laboratory (NRMRL) of the EPA is responsible for planning, implementing, and managing research, development, and demonstration programs to provide an authoritative, defensible engineering basis, this supports the policies, programs, and regulations of the EPA with respect to drinking water, wastewater, pesticides, toxic substances, solid and hazardous wastes, and Superfund-related activities. The Federal Energy Technology Center (FETC) of the Department of Energy (DOE) has responsibilities similar to NRMRL in that FETC is one of several DOE centers responsible for planning, implementing, and managing research and development programs. In June 1991, an Interagency Agreement (IAG) was signed between EPA and DOE that made funds available to support the Western Environmental Technology Office's operating contractor, MSE Technology Applications, Inc., and Montana Tech of The University of Montana for the development of the Mine Waste Technology Program (MWTP). This publication is one of the products of the research conducted by the MWTP through these two Federal organizations and provides a vital communications link between the researcher and the user community.

The objective of Activity IV, Project 1, is to establish the feasibility of using physical oxidation and tailings neutralization, in combination or separately, to accelerate and enhance the removal of dissolved metals from acid mine waters and to assess the possibility of recovering metals, such as copper, manganese, and zinc, from the water. This project will evaluate the effectiveness of the treatment process on water from the Berkeley Pit which is located in Butte, Montana, and will also consider the effectiveness, technical feasibility, and potential for technology transfer to similar sites in the United States.

Mention of trade names or commercial products does not constitute endorsement or recommendation for use by either of these agencies.

Executive Summary

This document addresses the technical results that were obtained in evaluating treatment technologies for remediating Berkeley Pit water.

The Berkeley Pit, which is located in Butte, Montana, was chosen for this project based on its unmatched volume of contained water and the quantity of metal pollutants present in the water. The hazardous constituents in the water are several orders of magnitude greater than discharge regulations. An understanding of the chemical properties of the Berkeley Pit water and the other sources of water that flow into the Berkeley Pit is required to develop and evaluate processes for successfully treating the water.

For this project, the chemistry study concentrated on speciation calculation, saturation with solids, neutralization, and oxidation. Initially, sulfate was realized as the dominant anion in the Berkeley Pit and iron as the major cation. An average of 50% of all metals in the water are complexed with sulfate. Most of the iron exists as ferrous ions, except near the surface where ferrous ions are oxidized and become ferric ions. This natural oxidation precipitates some of the iron and produces additional acid in the water.

During a series of several tests, Berkeley Pit water was also found to have a high oxidation potential. However, the kinetics of Fe(II) oxidation is strongly dependant on the pH of the water: the higher the pH, the faster the oxidation. Testing also revealed the Fe(II) in Berkeley Pit water is oxidized at a rate 50 times greater than pure Fe(II) in bicarbonate water. By adding sulfate, copper, and manganese, the oxidation slightly increases, with manganese having the greatest impact on the oxidation rate.

Berkeley Pit water also can be treated by using a two-stage neutralization process. Initially limestone and lime were used to neutralize the water to a pH of approximately 6 and to precipitate most of the aluminum and part of the iron and copper. During the second stage, the pH of the solution was raised to approximately 10.25 with aeration to precipitate the remaining metals. Sulfide precipitation was also effective as a pretreatment and metal recovery process. With this process, over 99% of copper and zinc was able to be removed at the first stage at a pH of 4.31.

Milling waste materials, such as lime mud and reject lime grits, dust from a cyclone and a baghouse, and fly ash, were also discovered to be successful in treating Berkeley Pit water. In addition, tailings slurry was used to lower the pH neutralization of Berkeley Pit water with the volume ratio of tailings slurry to the water watched closely.

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1. Introduction

This final report presents the information and results compiled by Montana Tech of the University of Montana for the Mine Waste Technology Program (MWTP), Activity IV, Project 1—Berkeley Pit Water Research Project. The research described in this report was conducted in accordance with the requirements of the Interagency Agreement (IAG), Activity IV, Scope of Work. The IAG was signed in June 1991 by the U.S. Environmental Protection Agency (EPA) and the Department of Energy (DOE) to initiate work on the MWTP. The work plan for the MWTP, Activity IV, Project 1, addresses testing and evaluating technology applicable to remediation of the EPA Technical Issue: Mobile Toxic Constituents—Water. The analytical methods and bench-scale treatment testing conducted for this study were consistent with the requirements of the EPA as outlined in the project-specific Quality Assurance Project Plan (QAPP) for Berkeley Pit water Bench-Scale Testing (Ref. 1). This final report describes the work conducted and reports the technical results obtained to evaluate treatment technologies for Berkeley Pit water. Refer to the QAPP for the detailed descriptions of the process operations.

1.1 Background

Located at the northwest edge of Butte, Montana, the Berkeley Pit, which contained copper and other metals, was one of the world's largest ore deposits (Figure 1-1). In the late nineteenth century, mining began in the Butte area. The Anaconda Copper Mining Company initiated open-pit mining in 1955. During the mining operation, drainage water was pumped from the mines and the Berkeley Pit, treated, and discharged; however, since the closure of the Berkeley Pit in 1982, the drainage pumps have been turned off, causing underground mine workings and the Berkeley Pit to flood with water.

The oxidation and leaching of sulfide minerals in the mines and in mine wastes by the water and the air are the major causes of acid mine drainage. In terms of contained volume of water and quantity of metal pollutants, the Berkeley Pit is unmatched by any acid-producing mine in the United States and possibly in the world. The Berkeley Pit has been filling with water at a rate of 5 to 7.6 million gallons per day, thus accumulating over 20 billion gallons of water to date. At this rate of accumulation, the water will reach an exposed alluvium bedrock contact in the Pit wall by the year 2011 and could, therefore, create a serious threat to the groundwater quality in the Butte area. Approximately one-third of the water entering the Berkeley Pit is surface water, and two-thirds of the water is groundwater.

The hazardous constituents in the water are several orders of magnitude greater than discharge regulations, and they clearly need to be removed and disposed of properly. To develop or to evaluate processes for treating the water requires an understanding of the chemical properties of Berkeley Pit water and the other sources of water that flow into the Berkeley Pit. For this project, the chemistry study concentrated on speciation calculation, saturation with solids, neutralization, and oxidation.

1.2 Research Objectives

The objective of MWTP, Activity IV, Project 1, is to establish the feasibility of using physical oxidation and tailings neutralization, in combination or separately, to accelerate and enhance the removal of dissolved metals and to assess the possibility of metals recovery of such species as copper, zinc, and manganese.

This project will identify and develop appropriate techniques for treating acid mine waters by evaluating methods of producing acceptable

water, depositing waste solids safely, and recovering valuable metals. Along with evaluating the effectiveness of the treatment process on Berkeley Pit water, this project will

evaluate various approaches by considering the effectiveness, technical feasibility, and the potential for technology transfer to similar sites in the United States.

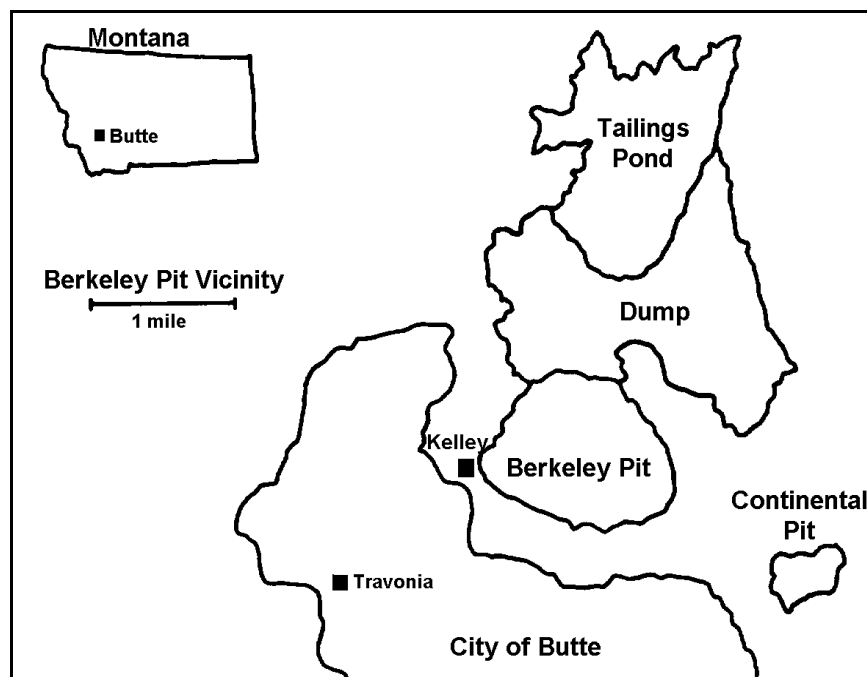


Figure 1-1. The Berkeley Pit and its surrounding area.

2. Chemistry

The chemistry of Berkeley Pit water was studied to determine which treatment processes would be most effective. Unlike most water that is anionically dominated by chloride or carbonate, the dominant anion in Berkeley Pit water is sulfate. Sulfate waters are usually associated with metal or coal mining wastes or with current geothermal activity. Berkeley Pit water also contains extremely high levels of dissolved heavy and transition metals with the major cation being iron. The chemistry study was based mostly on the reports from A. Davies (Ref. 2) and water samples taken by Montana Bureau of Mines and Geology (MBMG) in 1991 and 1992 (Ref. 3,4) for treatability studies.

The STABCAL computer program was used to calculate speciation of aqueous species and solubilities of solids and to construct various diagrams (Ref. 5). Most of the data, including adsorption results, were taken from MINTEQA2 (Ref. 6). Data for solid $\text{Fe}(\text{OH})_2$ was taken from the NBS Tables of Thermodynamic Properties (Ref. 7).

2.1 Composition of Berkeley Pit Water

Berkeley Pit water has been sampled and analyzed by the EPA, MBMG, and Montana Tech since 1984. The results of the water analysis of samples taken on various dates and at various depths from surface are listed in Table

2-1. Since 1986, the metals concentrations either remained relatively the same or slightly increased with time. Table 2-2 summarizes drinking water regulations, Industrial Effluent Standards for Ore Mining and Dressing for Metals Species [Code of Federal Regulations (40 CFR 440)], Gold Book standards, and the concentrations of the analytes of interest in Berkeley Pit water sampled in October 1993. The CFR 440 also served as the QAPP project objective of this research. Samples used for the experiments conducted for this project were collected in October 1993.

2.2 Sources of Water and Contaminants

Underground mining, which began in Butte in the 1870s, developed into a major operation by the late 1880s and flourished until 1974. Open-pit mining continued in the Berkeley Pit until 1982. During Butte's mining era, the water that accumulated in the mines and the Berkeley Pit was pumped and treated. Due to years of pumping, a hydraulic cone developed around the Berkeley Pit that caused, and continues to cause, most of the water in the surrounding areas to flow into the Berkeley Pit.

Like most acid mine drainage, the majority of the contaminants is the result of reactions between metal sulfides in the deposit and oxygen from air and water. Whether the source is surface water or groundwater, most water flows through the ore deposit, mine working, or waste rock dump before discharging into the Berkeley Pit. Water samples taken from surrounding areas were all acidic and contaminated with heavy metals (Table 2-3).

2.3 Concentration Profile with Depth

The most extensive analysis of Berkeley Pit water was conducted by the EPA in 1987 and reported by A. Davies (Ref. 2) and listed in Table 2-4. Water samples were taken at various depths from the surface. In general, the deep water (more than 100 feet below the surface), which represents the bulk of the water, has relatively uniform metal concentrations. The shallow water (less than 3 feet below the surface) is more acidic and has much lower metal concentrations, with the exception of the ferric ion which is higher in the oxidizing environment. The E_H (potential against hydrogen electrode) is also much higher in Berkeley Pit water at a depth of 3 feet. A water sample taken at the surface in October 1992 had an E_H of 880 millivolts (mV) and a pH of 2.57, while the water at 200 feet below the surface had an E_H of 621 mV and a pH of 2.96.

See the E_H -pH diagrams of iron-sulfur systems in Figures 2-1 and 2-2.

Near the surface, atmospheric oxygen causes iron to be oxidized from ferrous to ferric, which subsequently forms a solid hydroxide such as goethite ($FeOOH$) or ferric hydroxide ($Fe(OH)_3$). As the solid particles form, they tend to adsorb or coprecipitate other metals. Eventually, the particles sink and result in lower metal concentrations at or near the surface. According to an analysis of frozen surface water conducted by the MBMG in 1992, winter freezing may also contribute to the lower surface metal concentrations.

2.4 Concentrations of Elements in Berkeley Pit Water

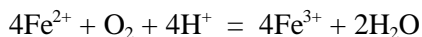
The Berkeley Pit water contains high levels of soluble contaminants (ionic strength is approximately 0.16 molal) and is anionically dominated by sulfate. Iron (Fe) is the dominant cation in Berkeley Pit water at a depth of 200 feet; however, because the ore deposit contains many different metals that readily dissolve in an acidic solution, aluminum (Al), calcium (Ca), copper (Cu), magnesium (Mg), manganese (Mn), and zinc (Zn) are also present at high concentrations (Table 2-1). The water contains high levels of heavy and transition metals (Fe, Zn, Cu, Al, and Mn) and alkaline earth metals (Ca and Mg) and low levels of more commonly dissolved alkaline metals [potassium (K) and sodium (Na)]. Surprisingly, the levels of As and Pb are quite low.

To evaluate the potential role of precipitation, it is instructive to divide metal ions according to their degrees of saturation (concentration versus solubility). Group one elements are those that are near saturation with their solid minerals, and group two elements are far below saturation. The following interpretations use data from Reference 2.

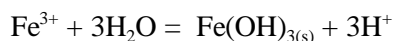
2.4.1 Elements Near Saturation

Ferric Ion and Aluminum

Iron is one of the most important cations in Berkeley Pit water. Total concentration ranges from 185 parts per million (ppm) near the surface to 1,060 ppm at a depth of 200 feet. Most of the iron exists as ferric (Fe^{3+}) near the surface due to the oxidation of ferrous (Fe^{2+}) as:



Aqueous ferric ion is less stable and precipitates as ferric hydroxide or sulfate salts, consequently producing acid as:



However, an equilibrium is developed because the formation of acid lowers the pH of the water and prevents further precipitation. The concentrations of the ferric ion in Berkeley Pit water lay between the thermodynamically calculated solubilities of FeOOH and $\text{FeO}(\text{OH})_3$ and agree with other research findings (Figure 2-3). The ferric ion concentrations are also close to the solubility of jarosite ($\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$).

The concentration of Al is 101 ppm near the surface and 193 ppm at a depth of 200 feet. The water is near saturation with respect to alunite ($\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$).

Potassium and Lead

The concentration of K in Berkeley Pit water varies from 11 ppm near the surface to 18 ppm at a depth of 200 feet. These levels are quite low compared to the underground mine waters in the surrounding areas near the Berkeley Pit. The formation of jarosite ($\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$) and alunite in Berkeley Pit water probably lowers the concentration of K.

The Berkeley Pit water contains a surprisingly low level of lead compared with other ore metals.

The Pb concentration varies with depth (0.112 ppm near the surface and 0.522 ppm at a depth of 200 feet). Based on thermodynamic calculation, the Pb in the water is saturated with respect to lead jarosite.

Calcium and Silica

The concentration of Ca in Berkeley Pit water ranges from 429 ppm near the surface to 482 ppm at a depth of 200 feet. In addition, the water is slightly saturated with respect to gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) formation. The solubility of gypsum is relatively insensitive to pH change, which explains why the concentration of calcium does not vary much with the varying depths of the water.

Berkeley Pit water has a silica concentration of 85 ppm near the surface and 51 ppm at a depth of 200 feet. The water is nearly saturated with the solubility of amorphous quartz. Like gypsum, the solubility of amorphous quartz is insensitive to pH below 5, which results in relatively stable silica concentrations at various water depths.

2.4.2 Elements Not Near Saturation

Ferrous Ion

Below the surface, most of the Fe exists as ferrous (divalent $\text{Fe}(\text{II})$) at a level of approximately 1,000 ppm indicating that Fe entering the Berkeley Pit is mainly in the divalent form. The water throughout the Pit is not saturated with respect to any ferrous solid.

Copper and Manganese

At a depth of 200 feet, Berkeley Pit water contains 200 ppm Cu and 220 ppm Mn. Both ions have concentrations slightly lower near the surface than at lower depths. Solubility calculations indicate that both metal ions do not approach saturation conditions with respect to their hydroxide or sulfate minerals. See Figure 2-4 for copper concentrations.

Manganese in solution is not derived from sulfide minerals but rather from carbonates and silicates from the ore deposit. These minerals are in acidic water without oxygen.

Zinc and Cadmium

Of the valuable metals in Berkeley Pit water, Zn has the highest concentration, ranging from 202 ppm near the surface to 497 ppm at a depth of 200 feet. The concentration of cadmium (Cd) is much lower, and ranges from 1.08 ppm near the surface to 1.87 ppm at a depth of 200 feet. Neither Zn nor Cd approaches saturation with respect to their hydroxide or sulfate minerals.

Magnesium and Sodium

Magnesium concentrations vary with depth, 149 ppm near the surface to 280 ppm at a depth of 200 feet. The concentration of Na is relatively low but much more uniform (about 70 ppm) than that of Mg. Neither metals are near saturating concentrations with respect to their hydroxide or sulfate minerals.

Arsenate and Arsenite

The Butte ore body contains a fair amount of arsenic (As) that occurs mostly as enargite (Cu_3AsS_4). The concentrate from the Berkeley Pit ore contained normally in the range of 0.75 to 3.5% As. The concentrations of arsenate [As(V)] and arsenite [As(III)] are surprisingly low compared to other metals in Berkeley Pit water (0.031 ppm near the surface and 1.15 ppm at a depth of 200 feet). These concentrations are not saturatable with any solid As minerals. The reasons for low concentrations may be due to two factors. First, before discharging into the Berkeley Pit, the As may be adsorbed by the clay minerals that are abundant in the ore deposit. Second, while in the Berkeley Pit, As may further be adsorbed by the precipitation of the ferric hydroxide (Figure 2-5).

2.5 Neutralization of Berkeley Pit Water

Although Berkeley Pit water contains high levels of

metals that provide high buffering capacity, the water can be neutralized with commonly used reagents.

2.5.1 Simulation of Berkeley Pit Water

Samples of deep Berkeley Pit water taken in 1992 (Table 2-1) were used to illustrate the buffering effects in both the computer simulation and laboratory tests. The equilibrium calculation indicated that the solution had an ionic strength of 0.1737 moles/liter and an imbalance charge of 0.009547 moles/liter. At the E_H and the pH of the water and the concentrations of other components, 10.57% of total iron is Fe(III) (equivalent to 113.15 ppm or 2.026 mM), and 89.43% iron is Fe(II) (957.78 ppm or 17.15 mM) according to the speciation calculation.

For titration simulation, the conditions of Berkeley Pit water included E_H , pH, and concentrations of all the components analyzed, including sulfur [S(VI)], silicon [Si(IV)], As(V), Cd(II), Cu(II), Al(III), Fe(II), Fe(III), Mg(II), Mn(II), K(I), Na(I), Zn(II), and Cu(II). The simulation assumed:

1. No charge transfer reaction for all the components involved, including the Fe(II)/Fe(III) couple.
2. The imbalance charge from the original water remains constant.

The simulation was performed by using STABCAL computer programs (Ref. 5). The species and thermodynamic data included in the calculation were taken primarily from MINTEQA2 (Ref. 6). Species included:

1. Aqueous species: all species listed in MINTEQA2 database.
2. Solid species: simple oxides, hydroxides, and gypsum listed in the MINTEQA2 database. These include $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, SiO_2 , As_2O_5 , $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$, $\text{Ca}_3(\text{AsO}_4)_2$, $\text{Cd}(\text{OH})_2$,

$\text{Ca}(\text{OH})_2$, $\text{Al}(\text{OH})_3$, $\text{Fe}(\text{OH})_3$, $\text{Mg}(\text{OH})_2$, $\text{Mn}(\text{OH})_2$, $\text{Zn}(\text{OH})_2$, and $\text{Cu}(\text{OH})_2$. Fe(OH)₂ was reported in NBS Tables of Thermodynamic Properties (Ref. 7).

3. The adsorption reaction of other species precipitates onto Fe(OH)₃ or FeOOH solids.
 - (a) Surface concentrations are 0.005 mole per mole Fe for site 1, and 0.2 mole per mole for site 2. The surface area of iron hydroxide is 53,400 m²/mole Fe, suggested by D. A. Dzombak (Ref. 8).
 - (b) The amount of Fe hydroxide available is not a constant, but is individually determined at each lime addition.

Figure 2-6 shows the results from a computer simulation by titrating with commonly used neutralization chemicals, including lime, limestone, caustic soda, magnesia, and soda ash. The amount of titrant added is represented by the moles of reagent added per liter of Berkeley Pit water. In adding limestone, the highest pH predicted was approximately 6; with magnesium hydroxide, the highest pH simulated was approximately 9. Both lime and caustic soda appeared to have the capacity to raise the pH above 10.

2.5.2 Lime Neutralization

The laboratory neutralization titration without aeration was performed using a 4-liter (L) beaker with 2 L of the deep Berkeley Pit water. An incremental amount of reagent was added to the water every 30 minutes. A set of these experiments was performed with slow agitation at 160 revolutions per minute (rpm), and another set of tests was performed with agitation at 500 rpm.

Results of lime neutralization from experimental testings and computer titration simulation are shown in Figure 2-7. The actual test results were lower than simulation results mainly because it was difficult to dissolve all the added lime in the water,

especially at low agitation speed and low pH levels. Small suspended lime particles were visible throughout the test. The results indicate the experiment was kinetically limited rather than thermodynamically limited.

2.5.3 Caustic Soda Neutralization

Results of caustic soda neutralization from experimental testings and computer simulation are presented in Figure 2-8. Compared to lime neutralization, neutralization with caustic soda displayed better agreement between the experimental results and results from computer

simulation. Caustic soda was more readily dissolved in the water, and thus, neutralization response was less dependent on agitation speed.

2.5.4 Magnesia Neutralization

Results of magnesium hydroxide neutralization from experimental testings and computer simulation were plotted in Figure 2-9. Both experimental and simulation indicate that by using magnesium hydroxide, the pH will not exceed 9. The resulting pH levels were not dependent on agitation speed.

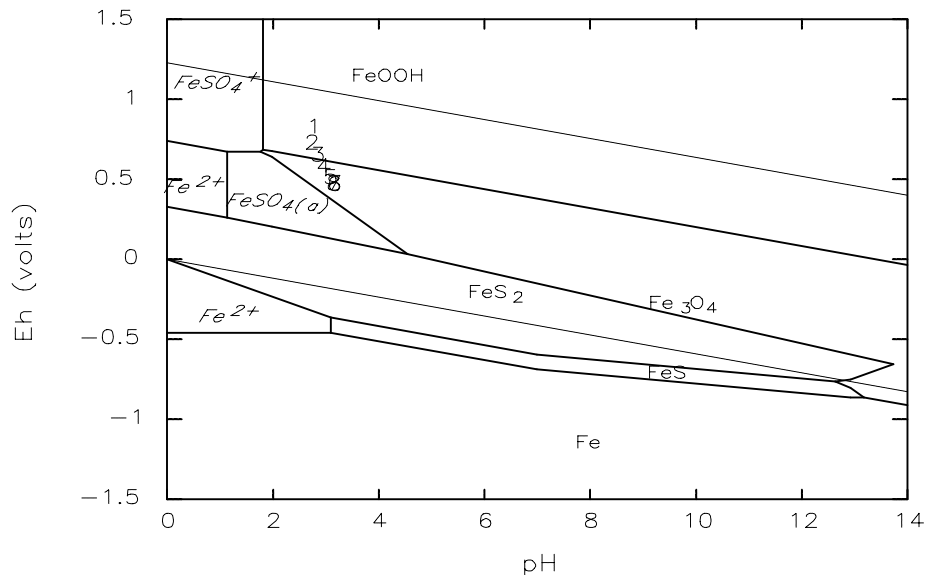


Figure 2-1. E_h -pH diagram of iron and its oxides and sulfides and Berkeley Pit water at various depths: 1(0), 2(3), 3(10), 4(50), 5(100), 6(200), 7(300), and 8(400 ft). Water samples were taken in October 1987.

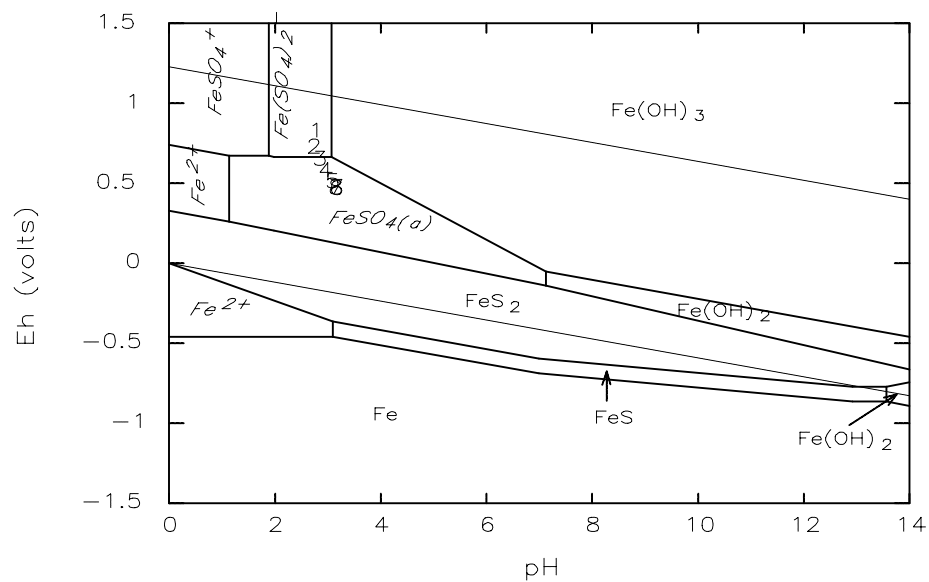


Figure 2-2. E_h -pH diagram of iron and its hydroxides and sulfides and Berkeley Pit water at various depths: 1(0), 2(3), 3(10), 4(50), 5(100), 6(200), 7(300), and 8(400 ft). Water samples were taken in October 1987.

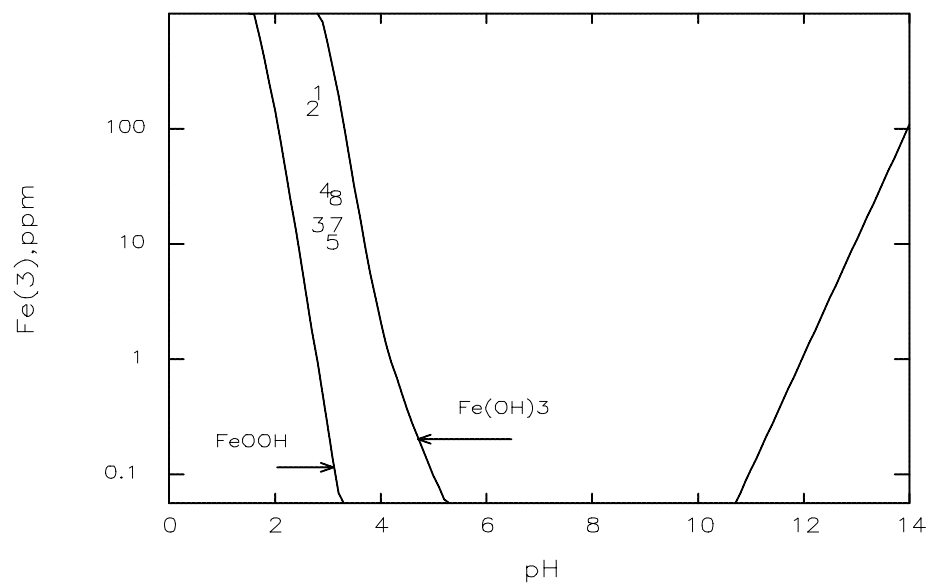


Figure 2-3. Solubilities of $Fe(OH)_3$ and $FeOOH$ as a function of pH and the concentrations of ferric iron in Berkeley Pit water at various depths: 1(0), 2(3), 3(10), 4(50), 5(100), 7(300), and 8(400 ft). Water samples were taken in October 1987.

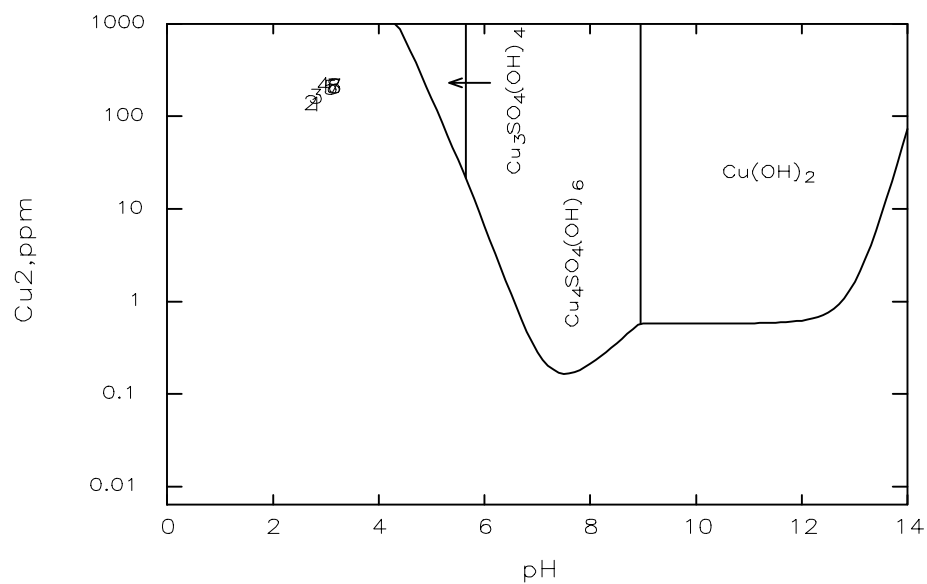


Figure 2-4. Solubilities of solids copper as a function of pH and the concentrations of copper in Berkeley Pit water at various depths: 1(0), 2(3), 3(10), 4(50), 5(100), 6(200), 7(300), and 8(400 ft). Water samples were taken in October 1987.

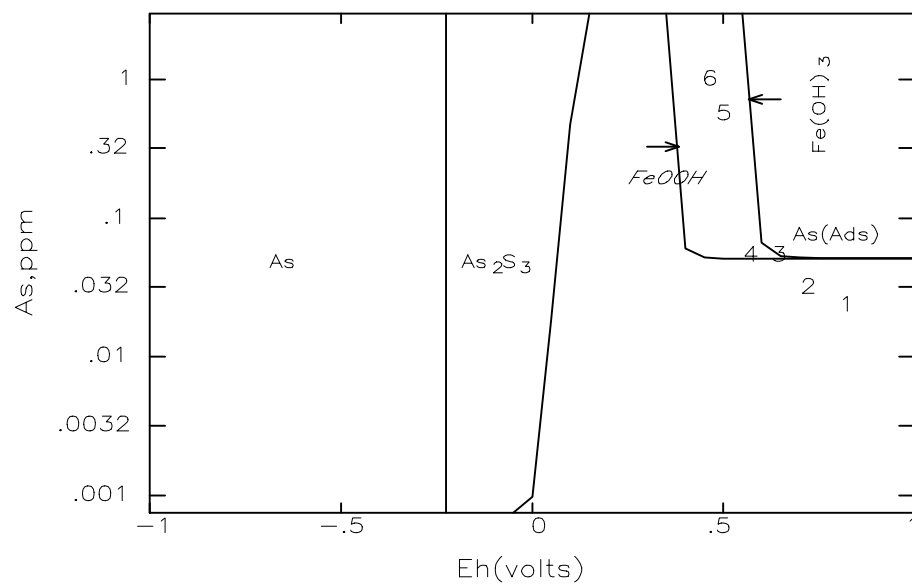


Figure 2-5. Solubilities and adsorption of arsenic as a function of E_h and the total arsenic (III and V) concentrations in Berkeley Pit water at various depths: 1(0), 2(3), 3(10), 4(50), 5(100), and 6(200 ft). Water samples were taken in October 1987.

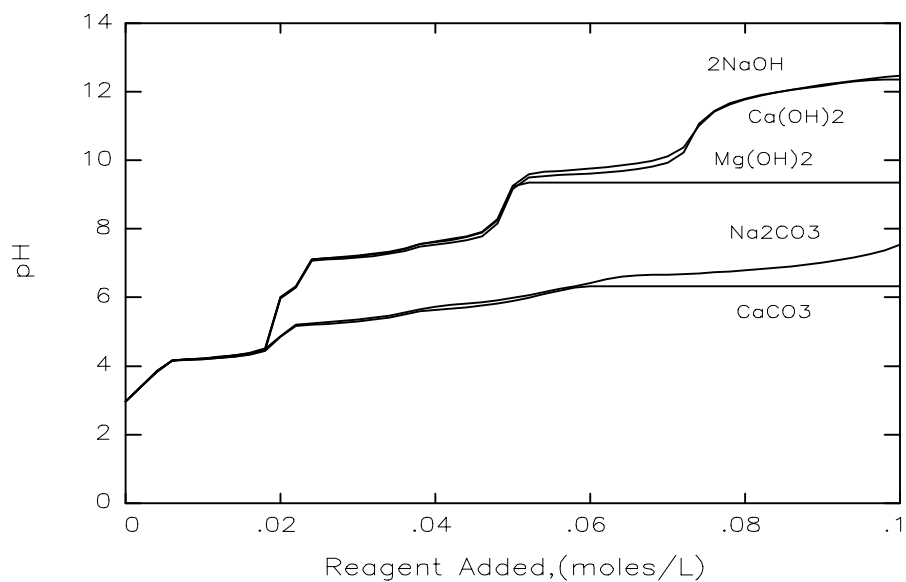


Figure 2-6. pH responses from computer simulation of neutralization of Berkeley Pit water (1992) using various alkaline reagents. To be able to match with other reagents, every mole of NaOH used is presented as $\frac{1}{2}$ mole to the X axis.

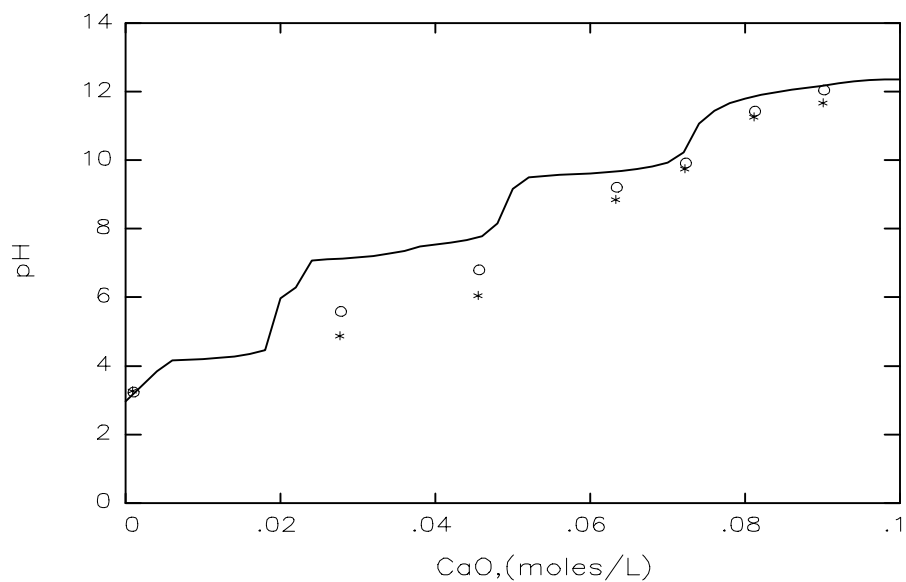


Figure 2-7. pH responses from computer simulation of neutralization of the Berkeley Pit (1992) water with CaO. The laboratory titration results are also shown as * for slow stirring speed at 160 rpm and o for fast speed at 650 rpm.

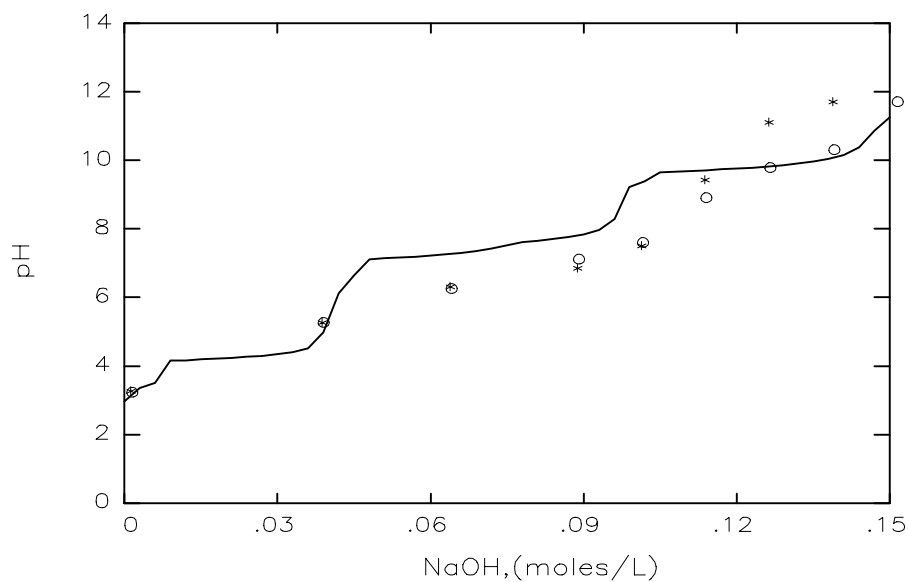


Figure 2-8. pH responses from computer simulation of neutralization of the Berkeley Pit (1992) water with NaOH. The laboratory titration results are also shown as * for slow stirring speed at 160 rpm and o for fast speed at 650 rpm.

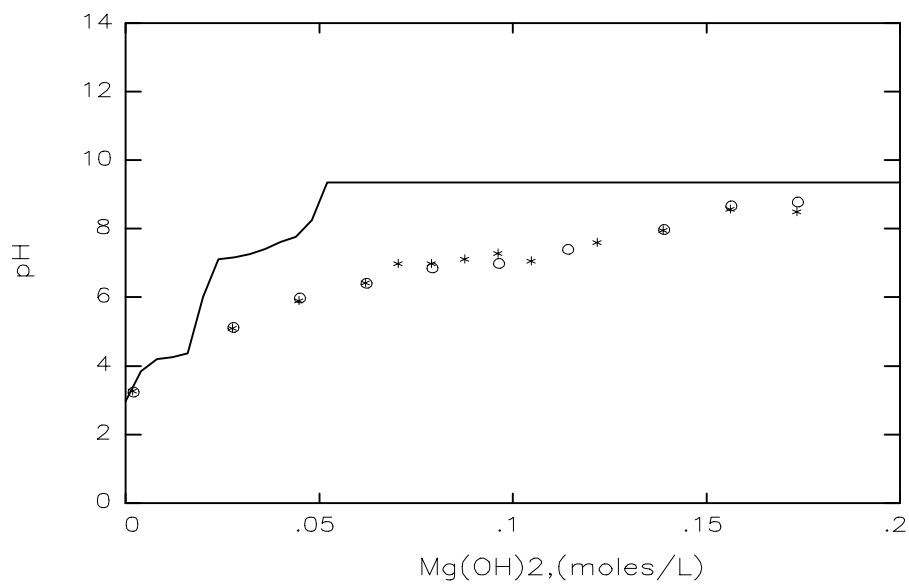


Figure 2-9. pH responses from computer simulation of neutralization of the Berkeley Pit (1992) water with Mg(OH)₂. The laboratory titration results are also shown as * for slow stirring speed at 160 rpm and o for fast speed at 650 rpm.

Table 2-1. Composition of Berkeley Pit water (in ppm) at approximately 200 feet below the surface over the years.

	Nov. 84 62 ft.	Jun. 85 100 ft.	Oct. 86 200 ft.	Oct. 87 216 ft.	May. 91 225 ft.	Oct. 92 200 ft.	Oct. 93 200 ft.
Al	142	172	192	193	288	304.5	301.3
As	0.2	0.43	0.04	1.2	0.83	0.43	0.084
Cd	1.54	1.62	1.74	1.76	1.57	2.00	2.215
Ca	477	435	457	479	492	525.1	477
Co			1.05	1.19	1.80		
Cu	164	229	204	202	191	215.1	214.2
Fe	256	451	918	1,010	1,088	1,112	1,167
K	4.4	8.8	24.3	18.7	20	19.9	17
Mg	236	261	291	279	418	517	441
Mn	106	116	144	161	182	225.5	224
Ni			0.91	0.99	1.05	0.91	
Na	61.7	60	65.8	70.5	68	107.7	77
Pb				0.66	0.08	<0.13	0.098
Zn	255	329	460	494	552	636.6	680
SiO ₂						51.24	0.115
Cl ⁻	12.3	8.3		21.8	10.9		25.3
F ⁻			8.4	19.2			34.9
SO ₄ ²⁻	4,410	5,550		6,940	8,010	7,700	8,092
pH	2.78	2.48		3.15	2.84	2.96	2.92
E _H , mV (SHE)				463	650	621	652

SHE (standard hydrogen potential)

Table 2-2. EPA Drinking Water Criteria, QAPP objective (ppm).

Element	Drinking Water (Primary)	Drinking Water (Secondary)	EPA Gold Book ¹	Project Objectives ²	Pit Water Oct. 93 (200 ft)
Al	NV	0.5-2.0	0.087	1	301.3
As	0.05	NV	0.19	0.5	0.084
Cd	0.005	0.01	0.0023	0.05	2.215
Cu	NV	1	0.042	0.15	214.2
Fe	NV	0.3	1	1	1,167
Mn	0.05	NV	NV	2	224
Pb	NV	0.05	0.010	0.3	0.098
Zn	NV	5	0.23	0.75	680

NV Not regulated.

¹ EPA Gold Book quality criteria for water 1986 and revision 1991. Some metal concentrations based on hardness of 250 ppm for aquatic life.

² Project Objectives: based on Code of Federal Regulations (40 CFR 440, 1988), Industrial Effluent Standards for Ore Mining and Dressing for Metal Species (monthly).

Table 2-3. Composition of water samples from surrounding areas (ppm).

	Alluvial Wells ¹	Bedrock Wells ²	Kelley Mine (deep) ³	Kelley Mine (surface) ⁴	Horse Shoe Bend ⁵	Berkeley Pit water ⁶
Al			204	2.15	282.5	304.5
As	0.008	0.039	17	1.42	<0.24	0.43
Cd	0.226	0.002		0.152	2.17	2.00
Ca			615	435	477.9	525.1
Cu	4.55	0.053		0.169	91.15	215.1
Fe	.096	14.6	4484	364	324.6	1112
K				31.4	8.69	19.9
Mg			790	152.	453	517
Mn	0.83	3.1	384.5	64.	168.6	225.5
Ni				0.14		0.91
Na				38.	76.62	107.7
Pb				0.005	<0.13	<0.13
Zn	22.96	1.57	801.5	153	354.59	636.6
SiO ₂				38.8	55.09	51.24
SO ₄ ²⁻				2598		7700
pH	5.55	6.28	3.3-3.7	5.44	3.23	2.96
E _H , mV (SHE)			490		691	621

1. Alluvial well water: Average from 3 wells, taken from February to May 91
2. Bedrock well water: Average from 3 wells, taken in May 91
3. Kelley Mine (surface water): about 800 feet from land surface, taken October 92
4. Kelley Mine (deep water): 3,500 feet from land surface, taken in July 93.
5. Horseshoe Bend water: surface water flows to the Berkeley Pit, taken in January 93
6. Berkeley Pit water: 200 feet below the surface, taken in October 92

Table 2-4. Berkeley Pit water taken and analyzed on October 1987 (Ref. 2): All concentrations are in ppm except As and Pb in ppb

Depth ft	0	3	10	50	100	200	300	400
Al	101	103	152	165	182	193	193	196
As Total	23	31	53	53	557	1,200	1,150	1,000
As (III)	1	1	0.5	0.5	42	72	87	101
As (V)	4	5	0.3	1.3	251	598	768	807
Cd	1.05	1.08	1.28	1.67	1.7	1.76	1.87	1.87
Ca	429	433	462	474	451	479	482	492
Cu	130	133	156	207	194	202	203	202
Fe Total	185	202	386	688	916	1,010	1,020	1,060
Fe(II)	0.25	60	262	622	900	938	958	962
Fe(III)	196	142	14	28	10	0	14	24
Mg	149	153	201	229	252	279	280	288
Mn	72	73.7	95.3	124	148	161	162	167
K	11.1	10.4	9.6	11.8	21.9	18.7	18.7	18.7
Na	73.5	73.1	71.7	70.2	67.5	70.5	70.8	72.2
Pb	112	112	149	273	562	668	522	665
Zn	206	212	280	387	451	494	497	512
Cl	9.94	9.82	9.14	9.26	19.9	21.8	22.1	28.7
SO ₄ ²⁻	4,190	4,850	5,740	5,960	7,060	6,940	6,760	11,600
SiO ₂	65.5	69.2	77.8	95.5	98.6	109	111	112
pH	2.8	2.7	2.8	2.95	3.08	3.15	3.15	3.14
E _H (mv, SHE)	820	720	643	570	500	457	468	463

3. Treatability

The experimental testing was divided into four major phases, including:

- C Physical Oxidation, Neutralization, and Metals Removal
- C Possibility of Metals Separation and Recovery
- C Neutralization Using Milling Wastes (tailings and tailings slurry)
- C Diverting and Treating Different Water Sources of the Berkeley Pit

Between October 1993 and July 1994, various experimental tests were conducted by the Montana Tech Metallurgical Engineering Department to treat Berkeley Pit water. Materials used in these tests included lime, limestone, magnesia, reject lime and lime grits, cyclone and baghouse kiln dusts, fly ash, tailings slurry, Berkeley Pit water, Kelley Mine water, and Horseshoe Bend water.

The physical oxidation and metal removal tests investigated the kinetics of primary oxidation at various pH values in Berkeley Pit water. In conjunction with the oxidation and hydroxide precipitation tests, the possibility of extracting valuable metals from Berkeley Pit water was also investigated. Tests on milling wastes investigated the possibility of treating the acid mine water with various sources of milling wastes, particularly the tailings and tailings slurry. In addition to tests that were completed using Berkeley Pit water, additional tests were conducted investigating the treatability of various sources of water that flow into the Berkeley Pit.

3.1 General Test Procedure

All laboratory tests for this project were bench scale and were conducted at room temperature in a 4-L polyethylene beaker equipped with an overhead stirrer. Normally, 2 L of solution were tested. The speed of the stirrer, normally maintained at approximately 150 rpm, was just enough to suspend the solids. If aeration was needed, two

fritted air diffusion tubes were immersed into the reaction vessel that introduced approximately 4 L of air per minute into the vessel. The pH and the E_H [(also known as oxidation/reduction potential (ORP))] of the solution were periodically measured and recorded. After each specified time period, approximately 25 milliliters (mL) of solution were sampled and filtered through a 0.45-micron membrane filter and then acidified at the time of collection with HNO_3 to a pH of less than 2. At the end of the test, the precipitates were either taken for settling tests or filtered and dried at 60 °C in an oven.

The settling test was performed in a 2-L graduated cylinder. The experiment and resulting calculations followed the modified Kynch method (Ref. 9). All the settling tests were performed without a settling aid.

For this bench-scale test, Berkeley Pit water samples taken in October 1993 (Table 2-1) from 200 feet below the surface were used. The sampled water, which was a light greenish color, was put into 5-gallon plastic containers and refrigerated at 4 °C or less before use. All samples had never been stored for more than 6 months.

Most of the chemicals used for the tests were reagent grade and purchased from either the Fisher Scientific Corporation or the VWR Scientific Corporation. Scrap iron used for copper cementation was supplied by Montana Resources Incorporated (MRI).

The majority of metal analyses were performed using an inductively coupled plasma spectrometer (ICP) [Varian, Liberty 100/200 ICP-Atomic Emission Spectrography (AES)] at MSE-HKM Laboratory in Butte. Some samples were also analyzed by using a graphite furnace Atomic

Adsorption, Perkin-Elmer 5100Z Flame Furnace Zeeman, by the Metallurgical Engineering Department at Montana Tech and by ICP [Perkin-Elmer Elan 5000 ICP-mass spectrometer (MS)] at the MBMG in Butte. Fe(II) was analyzed using the Colorimetric Bipyridine Method (Ref. 10) by Metallurgical Engineering Department personnel.

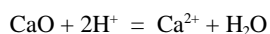
3.2 Neutralization and Precipitation

Acid neutralization is the method most commonly used to reduce acid-soluble heavy metals and other contaminants to acceptable levels. Alkalies commonly used to treat acid mine drainage are lime (CaO), limestone (CaCO₃), caustic soda (NaOH), soda ash (Na₂CO₃), and magnesium hydroxide (Mg(OH)₂). Because of the low cost and relatively easy operation, lime and limestone are the most widely used of these reagents. Since the solubility of the ferric ion (Fe³⁺) is less than the ferrous ion (Fe²⁺) and ferric hydroxide possesses better settling characteristics than the hydroxide, the neutralization processes are usually equipped with aeration to oxidize ferrous ion to ferric ion. Most of the metal ions (Al, Cu, Zn, Mn, Cd, and As) are either precipitated as ferrous hydroxides or coprecipitated with ferric hydroxide as adsorbed species.

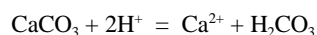
3.2.1 Chemistry of the Process

When lime or limestone reacts with acid mine drainage, the pH increases as the acids are neutralized. The heavy metals are removed from the solution through precipitation as metal hydroxides, and sulfate can be partially removed as gypsum. Overall reactions for these chemical treatment processes follow:

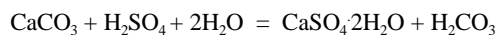
1. Acid neutralization with lime (CaO):



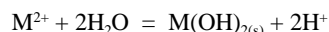
2. Acid neutralization with limestone (CaCO₃) at pH < 6:



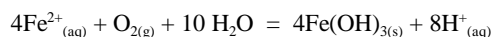
3. Sulfate precipitation with lime or limestone:



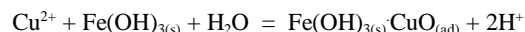
4. Metal ion precipitation as metal ion hydroxides:



5. Oxidation of Fe(II) and precipitation of Fe(III):

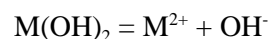


6. Adsorption and coprecipitation of metal ions with Fe(OH)_{3(s)}:



3.2.2 Solubilities of Metal Hydroxides

Precipitation of metal hydroxide is usually controlled by the equilibrium. The equilibrium concentration of the metal ions and the amount of solid precipitate is governed by the equilibrium constant that is normally expressed as solubility product, K_{sp}, such as the values reported in *Aquatic Chemistry* (Ref. 11) as:



$$K_{sp} = \{\text{OH}^-\}^2 \{\text{M}^{2+}\}$$

where { } represents the activity of an aqueous species. The activity is related to the concentration by the activity coefficient. Since simple M²⁺ forms various complexes with hydroxide ions and anions, such as sulfates, the concentration of M²⁺ is controlled by all the equilibrium and mass balance equations involved. The sum of the total concentrations of the metal ions, including complexes equilibrated with solid, is defined as the solubility of that solid. Figure 3-1 shows the thermodynamically calculated solubilities of major metals present in Berkeley Pit water (1992) as a function of pH.

3.2.3 Adsorption of Metals by Ferric Hydroxide

Iron and aluminum hydroxides have a well documented ability to adsorb trace metals from water. Ferric hydroxide, in particular, is capable of adsorbing both cations, such as Cd^{2+} , and anions, such as AsO_4^{3-} . The ferric hydroxide also has tremendous amounts of surface area (e.g., 600 square meters (m^2) per gram of iron hydroxide) and adsorption capacity of 0.2 moles per mole. The removal of one particular metal depends on the amounts of the adsorbent available, the pH of the water, and the competition among all the ions present in the system.

The adsorption reactions on ferric hydroxide, along with hydroxides precipitation for Berkeley Pit water as a function of pH, were simulated using the STABCAL program. The calculations were based on the chemical composition of the water measured in 1992. Species involved in the simulation of Berkeley Pit water (solid and aqueous and adsorbed by ferric hydroxide) and the adsorption capacity of ferric hydroxide are the same as mentioned previously (Section 2.5.1).

The simulated residual concentrations of As, Cd, and Pb due to precipitation with and without adsorption are plotted in Figure 3-2. The calculation assumed that 95% of ferrous ions were oxidized to ferric. The predictions show that metals such as arsenic are not removed by precipitation, rather by adsorption. In addition, adsorption removes Pd and Cd at lower pH levels.

3.3 Experiments

3.3.1 Oxidation of Berkeley Pit Water

The physical oxidation experiments evaluated and compared the kinetics of Fe(II) oxidation to Fe(III) in Berkeley Pit water. These tests also determined the effects of oxidation on the reagent requirements needed to produce the necessary increase in pH for metal removal by chemical precipitation. Although the oxidation rate was slow at a low pH, oxidation

and precipitation can be observed even in the untreated water. The results from air oxidation are presented on Figures 3-3, 3-4, and 3-5. Figure 3-3 shows the rates of oxidation at a pH of 5.5, 7.8, and 9.9. Figures 3-4 and 3-5 show the results of spiking Berkeley Pit water with sulfate and other ions including Cu, Mn, and Zn at a pH of approximately 5.6. The level of spiking was to double the concentration in the water.

The kinetics of ferrous oxidation was found to be strongly dependent on the pH of the water; a pH greater than 7.8 significantly enhanced the oxidation rate. Spiking with sulfate, Cu, or Mn increased the oxidation rate. The order of effect was $\text{Mn} > \text{sulfate} > \text{Cu}$. Zinc had no effect on the rate of oxidation.

The comparison of Berkeley Pit water with the simple ferrous bicarbonate water is shown in Figures 3-6a and 3-7 with two different initial Fe(II) concentrations (samples were taken at two different times). The oxidation rate for the ferrous bicarbonate water was calculated from the equation in *Aquatic Chemistry* (Ref. 11) that follows:

$$\frac{d[\text{Fe(II)}]}{dt} = k[\text{Fe(II)}][\text{OH}^-]^2 P_{\text{O}_2}$$

Where:

$$k = 8 \times 10^{13} (\text{min atm})^{-1} (\text{mol/L})^{-2}$$

P_{O_2} = partial pressure of oxygen

Shown in Figure 3-6b with two additional duplicated experiments, the results were consistent. Using data from 0 to 150 minutes, the first order plot, i.e., $\ln [\text{Fe(II)}/\text{Fe(II)}_{\text{initial}}]$ vs. time, revealed a rate constant of $5.88(\pm 0.04) \times 10^{15}$ for Berkeley Pit water. The value is approximately 75 times larger than that of a simple Fe(II) system.

3.3.2 One-Stage Neutralization

The one-stage neutralization test demonstrated metals removal by combining conventional

neutralization with various types of alkaline reagents and aeration.

Neutralization with Aeration

Two liters of Berkeley Pit water were placed in a 4-L plastic beaker. The reaction was started by adding the neutralization reagent, turning on the stirrer, and introducing air into the reactor. Three reagents (lime, limestone, and magnesia) were used to control the pH of the solution at different levels. After 2 hours, a 25-mL sample of solution was taken. The tests for one-stage neutralization included:

- neutralization with lime at a pH of 9.6, 10.2, and 11;
- neutralization with magnesia at a pH of 8.2 and 8.3; and
- neutralization with limestone at a pH of 6.5.

The testing conditions and results from critical tests are summarized in Table 3-1. The results indicated that one-stage neutralization with aeration was incapable of cleaning the water well enough to pass the discharge regulations listed in the QAPP in all cases. The results were compared to the effluent project objectives listed in the QAPP or to the National Drinking Water Standards when a project objective was not listed for that analyte. Because Al has a range of 0.05–2 ppm listed for the maximum contaminant level in the Secondary National Drinking Water Standards and the concentration of Al is approximately 300 ppm in Berkeley Pit water, 2 ppm was used when interpreting results.

Three tests were performed using lime to vary the pH of the solution. The first test, using lime to raise the pH to 9.6, successfully removed the metals of interest to levels below the QAPP project objectives effluent standards (Table 2-2). Aluminum apparently began to redissolve during the second test when the pH was raised to 10.2 using lime since Al concentration was greater than the QAPP effluent standards. All other metals (As,

Cd, Cu, Fe, Pb, Mn, and Zn) were removed to concentrations below the project objectives. The third test used lime to raise the pH of the water to 11.2. The concentration of Cd and Mn was above the QAPP effluent standards.

Two tests were performed using magnesia to raise the pH of the water to 8.2 and 8.3. Although the pH of the solutions were very similar, the second test used 4 grams per liter (g/L) more magnesium hydroxide, which resulted in lower metals concentrations in the filtrate compared to the first test using magnesium hydroxide. Both tests achieved the QAPP effluent standards exception of Mn in the first test.

The test using limestone (pH 6.5) showed the poorest metal removal capability. Because of low pH levels, all metal concentrations, except Al and As, were too high to pass QAPP effluent standard.

Except when using limestone (pH 6.5), results mostly passed secondary drinking standards. Compared to the Gold Book standards, concentrations of Al, Zn, Mn, and Cd were consistently higher in any pH.

Problems Related to One-Stage Neutralization

One-stage neutralization is a simple, effective, and proven technique used to treat acid mine drainage, particularly from coal mines. The problem with using this method to treat Berkeley Pit water is identifying the pH that would produce water able to satisfy Mn, Zn, and Cd regulations while meeting the Al regulation level. The solubilities of Mn and Al hydroxides, as a function of pH considering all the components from Berkeley Pit water, were computed and are shown in Figure 3-8. Judging from the diagram, the optimal pH needed to remove Al is between 6 and 7; however, this pH level is too low to remove Mn and Zn. When the pH is raised high enough to remove Mn (greater than 10), Al precipitates start to redissolve.

Several options were considered that have the potential to reduce metal concentrations to satisfy the discharge regulations for all metals. The first option was to separate the Al precipitates by controlling the pH at approximately 6 and then to raise the pH to over 10 to precipitate Mn. The second option was to separate the precipitates from treated water by one-stage neutralization and then to bring the pH back to about 6 to precipitate redissolved Al. The third and final option was to develop a process that would have the capacity to reduce the precipitation pH for Mn; for example, improving the absorption effects by increasing the concentration of ferric ions in the solution would be accomplished.

3.3.3 Two-Stage Neutralization

Metal hydroxides associated with Berkeley Pit water precipitate at various pH levels. A two-stage neutralization method was therefore proposed and investigated. The purpose was to precipitate most of Fe(III), Al, and Cu at a pH of approximately 6. After separating the precipitates from the water, the pH of the filtrate was raised to between 10.25 and 10.5 to remove the remaining metals, including Zn, Mn, and Cd.

Test conditions were as follows:

- C first-stage neutralization with lime or limestone at pH of 6.4 and 5.6, respectively; and
- C second-stage neutralization with lime at pH about 10.

Results and Summary

The testing conditions and analytical results from two critical two-stage neutralization tests conducted for this project are summarized in Table 3-2. Using the reagents and conditions stated, two-stage neutralization was able to remove metals to achieve the QAPP effluent standards and the secondary drinking water standards, except for Mn, residual metal concentrations also passed Gold Book standards. The concentration of Cd was

under the detection limit of 0.003 milligrams per liter (mg/L), which was slightly higher than the Gold Book requirement of 0.0023 mg/L.

For comparison, Table 3-2 also lists the results from Berkeley Pit water (2 liter and 50 gallon) using the two-stage neutralization technique performed in 1993 (Ref. 4). The results analyzed with ICP-MS generally agreed with this research experiment. Both Mn and Cd were found to be below the detection limits of 0.001 mg/L, which past the Gold Book standards.

The pH of the first stage was kept at approximately 6. Lime and limestone were both effective. Limestone, however, was probably the better choice since it controlled and buffered the pH of Berkeley Pit water at a pH of 6. In addition, limestone produced faster settling and more filterable sludge. A small amount of lime could be added along with limestone if limestone alone could not raise the pH high enough.

Aeration was necessary during the second stage of neutralization; lime was effective for the second stage in both tests. The pH of the second-stage neutralization should be between 10 and 10.5; however, 10.25 would be an optimal pH. For this project, a pH of greater than 10.5 would also be acceptable if the pH of the first stage could be slightly higher than 6 to remove as much Al as possible.

3.3.4 Large-Scale Two-Stage Neutralization Test

The two-stage neutralization method was tested and verified by using 10 L of Berkeley Pit water. The experimental testing included the following four sequential steps.

1. Aeration of original water without neutralization.
2. Low pH neutralization without aeration.

3. High pH neutralization with aeration.
4. Reacidification of final solution to neutral pH.

All samples for this test were analyzed by the MBMG. The analytical data included not only the concentrations of metal ions but also the concentrations of counter ions, such as sulfate, chloride, etc. A complete listing of the test conditions and results are available in Table 3-3. All of the metals concentrations met the QAPP effluent objectives and the secondary drinking water standards.

3.3.5 Sulfide Precipitation and Neutralization

Sulfide precipitation, as a pretreatment process, is one of the common methods used to remove metal ions from solution by forming low solubility metal sulfides. In the sulfide precipitation process, a soluble sulfide reagent was added to Berkeley Pit water causing the sulfide minerals, such as pyrrhotite (Fe_{1-x}S) and sphalerite (ZnS), to precipitate.

One and two-stage sulfide precipitation tests were performed using sodium sulfide ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$) and lime (CaO). In the one-stage test, sodium sulfide and lime were added together to raise the pH to approximately 10. At a pH of 10, the concentration of hydroxide ions was high enough to cause virtually all dissolved metals, except aluminum, to precipitate as insoluble metal hydroxides. In the two-stage test, sodium sulfide was added in the first-stage, and after separating the precipitates, lime was added to the filtrate along with aeration to raise solution pH to approximately 10 to remove the remaining metals.

Results and Summary

In the sulfide precipitation process, solution pH was controlled by lime addition. Copper, Cd, Zn, and ferrous ions were precipitated as sulfides. Compared to the metal hydroxide precipitation process, using sulfide precipitation precipitated Cd

and Zn at lower pH. The results are listed in Table 3-4. As seen in the table, both one and two-stage sulfide precipitation processes were effective in removing both the Al and Mn simultaneously to achieve the QAPP effluent standards for Mn and the secondary drinking water standard for Al. As a pretreatment and metal recovery process, over 99% of the Cu and Zn were recovered at the first stage using sodium sulfide at a pH of 4.3. The results are shown in Table 3-5. Drawbacks to using sulfide precipitation and neutralization include the tremendous amount of H_2S gas that is released during this process and the fact that the sludge generated from this process showed very poor filtration characteristics.

3.3.6 Copper Cementation Prior to Neutralization

Among the metals present in Berkeley Pit water, Cu (over 200 ppm) is probably the most valuable. The cementation test was conducted to investigate the possibility of using scrap iron to produce cement copper and to identify any ill effects caused by the cementation conducted in the subsequent neutralization step. The results will be used to determine the effectiveness of the treatment processes and to calculate the Fe consumption.

The cementation operation was, and still is, practiced near the Berkeley Pit by taking the leach water that percolated through the waste rock dumps during mining activities at the Berkeley Pit. MRI, which currently mines the Continental Pit and mills in the Weed Concentrator, also operates the leach-precipitation plant. Berkeley Pit water, in fact, contains a higher Cu concentration than the leach solution found in the leach-precipitation plant.

Copper Cementation with Scrap Iron and Iron Filings

The cementation test was performed by using scrap iron and iron filings. Scrap iron, provided by MRI, was first cut to 1-inch square and then soaked in 10% hydrochloric acid (HCl) for 2 days to remove the plastic film, thus allowing the Cu in solution to cement to the Fe. Every 30 minutes, approximately 25 mL of solution were withdrawn from the reaction vessel and filtered for analyses. The results shown in Table 3-6 indicate that Cu recovery from Berkeley Pit water with scrap iron and iron filings depends on the retention time. Two hours of retention time were enough to remove over 87% of Cu from Berkeley Pit water; however, the dissolved Fe in the water was greater than the stoichiometric consumption for the recovered Cu. This overconsumption may be attributed to dissolution of the scrap iron and iron filings by the acidic water itself.

Neutralization after Copper Cementation

The effectiveness of neutralization after Cu cementation with scrap iron was examined. The solution was subjected to the two-stage neutralization method. The resulting metal concentrations in the filtrate are listed in Table 3-7. As shown in the table, two-stage lime neutralization after Cu cementation still has the capacity to treat Berkeley Pit water to meet the QAPP project objectives and the secondary drinking water standards where applicable. Tests confirmed that the Cu cementation process using iron filings and scrap iron does not have any harmful effects on the subsequent neutralization treatment processes.

3.3.7 Treatment of Inflow Water

In addition to Berkeley Pit water, this project also investigated the treatabilities of various sources of water that flow into the Berkeley Pit, mainly the surface water and underground mine water from the Kelley Mine and from the Horseshoe Bend. If proven to be feasible and successful, alternative methods may involve intercepting and treating the water before it enters the Berkeley Pit. Tests for

various sources of water included two treatment options:

- conventional one-stage lime neutralization; and
- nonconventional two-stage hydroxide precipitation.

The experimental testing on the Kelley Mine and Horseshoe Bend water followed the testing procedures described in Sections 3.3.2 and 3.3.3 of this report. Lime was used for all the tests, although limestone was tested for the first-stage of the two-stage neutralization. The analytical results for critical samples of one and two-stage neutralization are listed in Tables 3-8 and 3-9, respectively.

As seen in Tables 3-8 and 3-9, one-stage neutralization for treating the Kelley Mine and Horseshoe Bend water had the same problem as those found when treating Berkeley Pit water. Aluminum redissolved at the high pH levels necessary to remove the Mn. Two-stage neutralization still had capacity to treat the Kelley Mine and Horseshoe Bend water to meet project objectives, except for Zn. The results, however, meet the secondary drinking water regulations. It is important to notice that the ratio of Fe/Mn in the Kelley Mine water (over 10) was much higher than that in Berkeley Pit water (approximately 5). High Fe concentration in the Kelley Mine water increased the adsorption effects, and as a result, Mn was removed at a relatively lower pH, which was beneficial to Al removal. In this case, however, the Fe/Mn ratio was still not high enough to satisfy both Al and Mn at the same time to meet project objectives or drinking water regulations.

To obtain the optimized Fe/Mn ratio and to understand the absorption of ferric hydroxide, further tests would be required to examine different Fe/Mn ratios by adding ferric ions to the water. The results would be applied to the treatment processes by one-stage neutralization.

3.3.8 Treatment of Berkeley Pit Water Using Milling Wastes

The work described in this section investigated the possibility of treating the acid mine drainage with various sources of milling waste products. The materials used included: reject lime mud and lime grits from a paper mill, cyclone and baghouse kiln dusts from a lime calcination plant, fly ash from a power plant, and tailings slurry from the MRI Concentrator.

The experimental tests for the milling wastes were divided into two areas:

- titration of Berkeley Pit water with milling wastes; and
- treatment of Berkeley Pit water with the addition of milling wastes.

Titration of Berkeley Pit water with Milling Wastes

Tests were conducted by adding an incremental amount of milling waste into 2 L of Berkeley Pit water every 15 minutes without aeration. For tailings slurry, there were two options. Option 1 included adding the tailings slurry to Berkeley Pit water, and Option 2 involved adding Berkeley Pit water to the tailings slurry. The solution pH and E_H were recorded every 15 minutes. The pH changes in Berkeley Pit water were plotted in Figures 3-9, 3-10, and 3-11. The conclusions from titrating Berkeley Pit water with the milling wastes include the following:

1. Reject lime mud and lime grits are weak alkalies, and both behave like limestone. The limestone has a capacity to raise the pH of the water to approximately 6.
2. Kiln dusts from cyclone and baghouse and fly ash are strong alkalies, and both behave like lime. The lime is capable of raising the pH of the water to 11.
3. Tailings slurry has a high pH value but is a weak alkaline reagent.

Treatment of Berkeley Pit water with Milling Wastes

After the titration tests were performed on all kinds of tailings and tailings slurry, Berkeley Pit water was neutralized with milling wastes. The experimental plan included one and two-stage neutralization. Since the reject lime mud and lime grits are weak alkalies, they were used to partially replace lime. Since kiln dusts from cyclone and baghouse and fly ash are strong alkalies, they were used to totally replace lime. The tailings slurry was tested with the following ratios of slurry to Berkeley Pit water: 0.1, 0.2, and 0.3. Lime was only used to raise the pH to a desired level if the milling wastes could not achieve the desired pH. The lime equivalent of the milling wastes in the one and two-stage neutralization are tabulated in Table 3-10.

Besides their abilities of replacing part of lime consumption to neutralize Berkeley Pit water, these milling wastes also improved the settling characteristics of the sludge formed.

3.3.9 Copper Cementation Following Pretreatment with Tailings Slurry

Some experiments were conducted to reduce the scrap iron consumption in the Cu cementation process. Berkeley Pit water was pretreated by tailings slurry at the ratios of 0.05, 0.10, and 0.15 L per L of Berkeley Pit water. The subsequent test procedure of the Cu cementation followed the description in Section 3.3.6 of this report. The results for Cu cementation following pretreatment with tailings slurry are listed in Table 3-11.

Pretreatment with tailings slurry reduced the Fe concentration in Berkeley Pit water. After the Cu cementation, the final Fe concentration in the water was almost the same as that without pretreatment using tailings slurry. The results indicated the pretreatment process using the tailings slurry increased the Cu recovery (over 97% of the Cu was cemented during 2 hours, compared with 87% in the previous tests without pretreatment with tailings slurry) but also increased the scrap iron consumption.

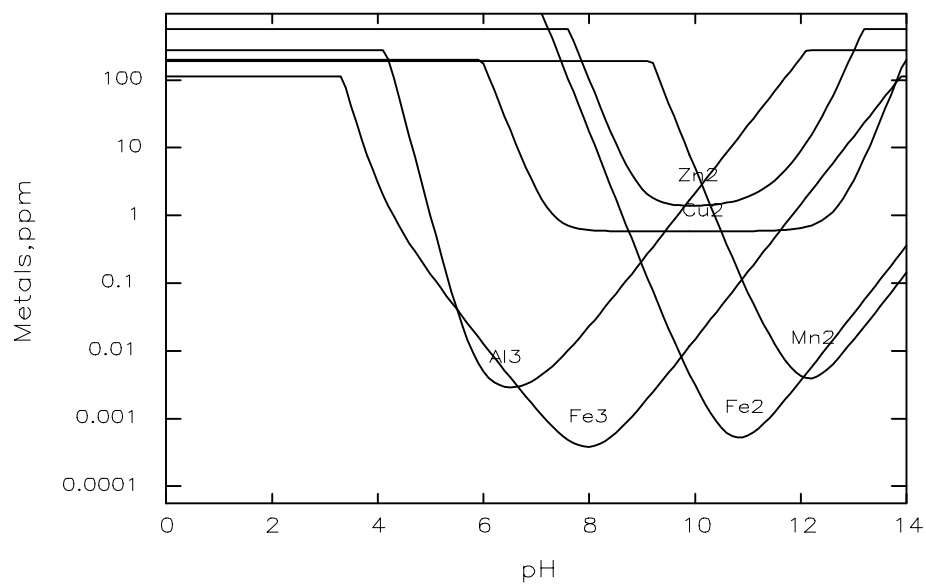


Figure 3-1. Calculated solubilities of selected metals versus pH from Berkeley Pit water (1992).

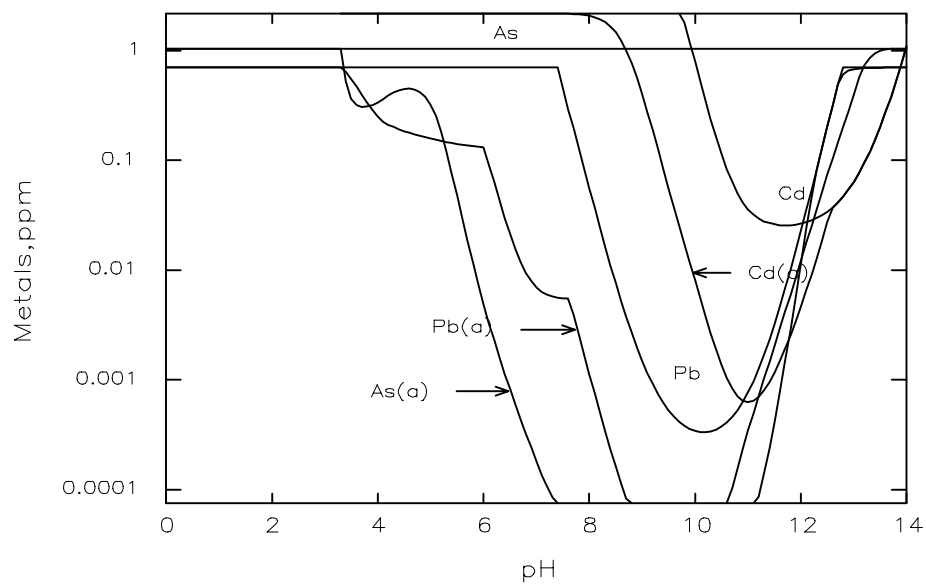


Figure 3-2. Concentrations of As, Cd, and Pb versus pH with and without considering the adsorption onto iron hydroxide surface. Precipitation plus adsorption is labeled with (a). Calculation is based on the water sample taken in October 1992. Not plotted, adsorption also includes H^+ , OH^- , SO_4^{2-} , Zn^{2+} , Cu^{2+} , and Ca^{2+} .

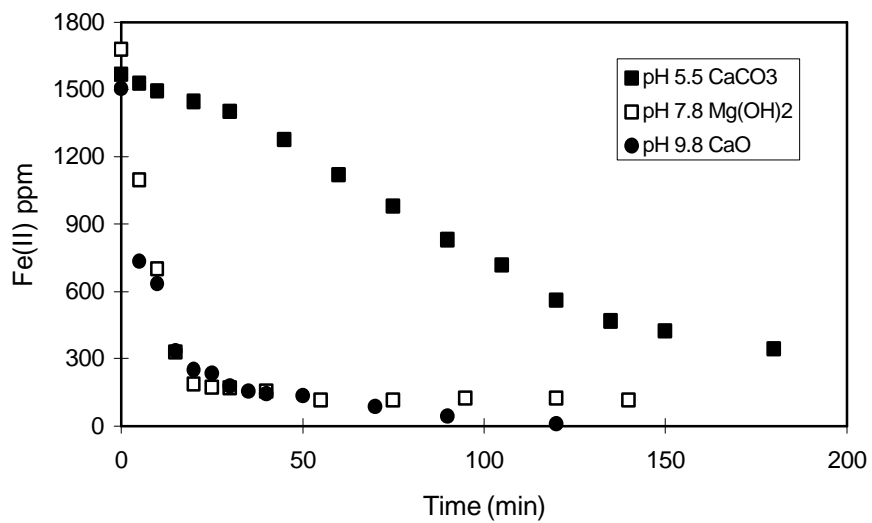


Figure 3-3. Fe(II) oxidation as a function of time and pH. The various pH levels were achieved by adding CaCO₃ for pH 5.5, Mg(OH)₂ for pH 7.8, and CaO for pH 9.8.

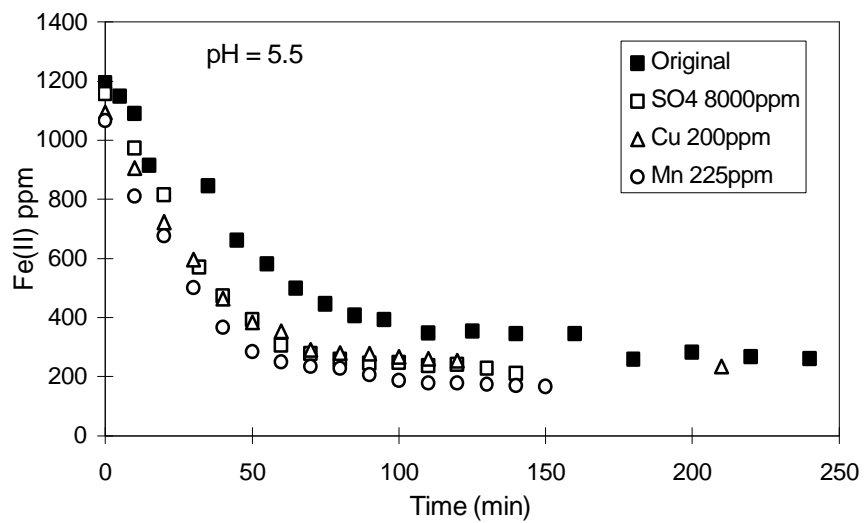


Figure 3-4. Fe(II) oxidation as a function of time exposed to different spiking reagents. The additional spiking concentration was the same as the concentration in the original water.

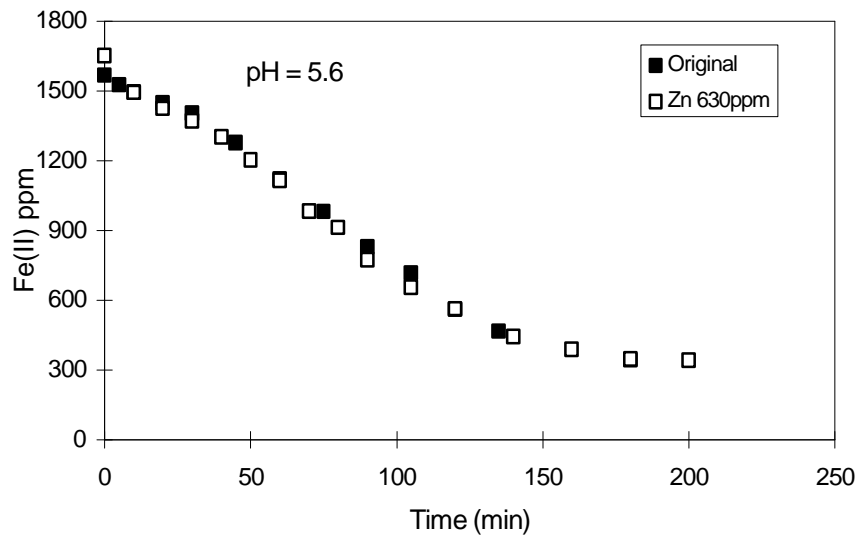


Figure 3-5. Fe(II) oxidation as a function of time exposed to Zn spiking reagent. The additional concentration was the same as the concentration in the original water.

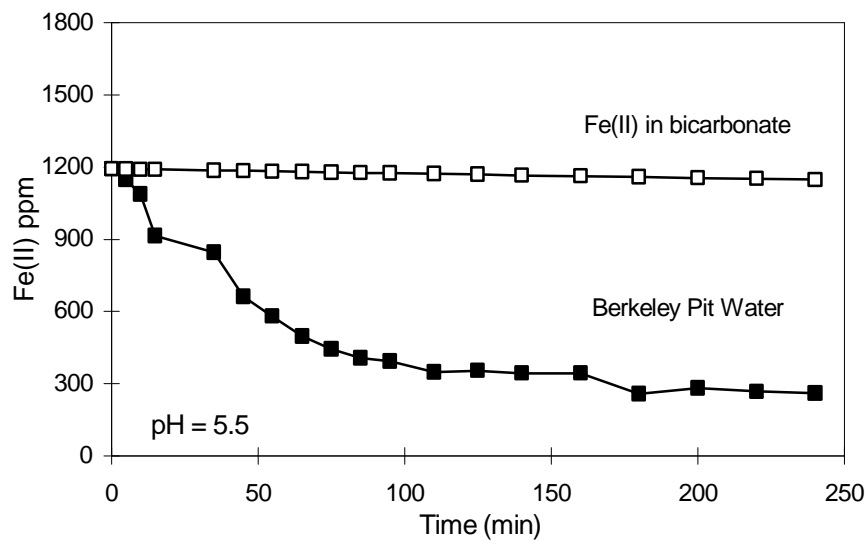


Figure 3-6a. Fe(II) oxidation as a function of time in the Berkeley Pit compared to the bicarbonate system computed from the literature (Ref. 11). The initial Fe(II) concentration was 1,193 ppm.

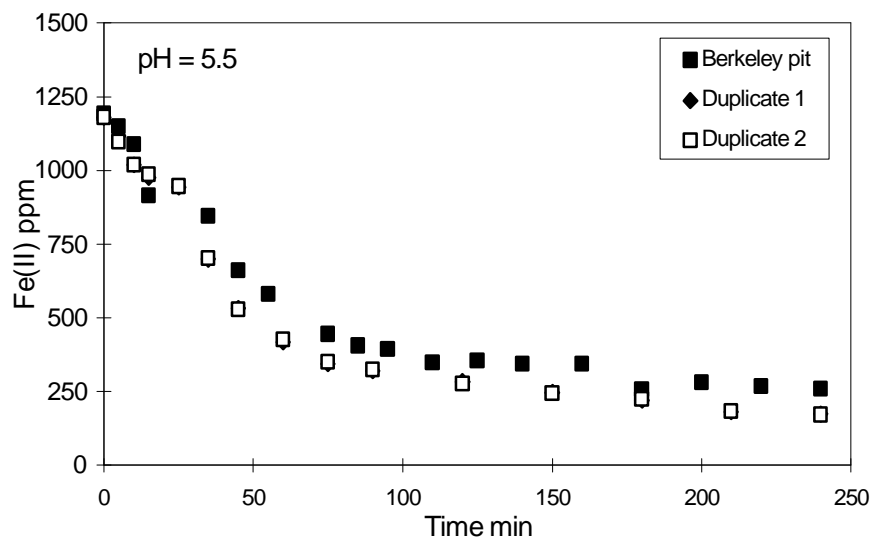


Figure 3-6b. Duplicated test results from Fe(II) oxidation as a function of time in Berkeley Pit water. Initial Fe(II) concentration was 1,193 ppm.

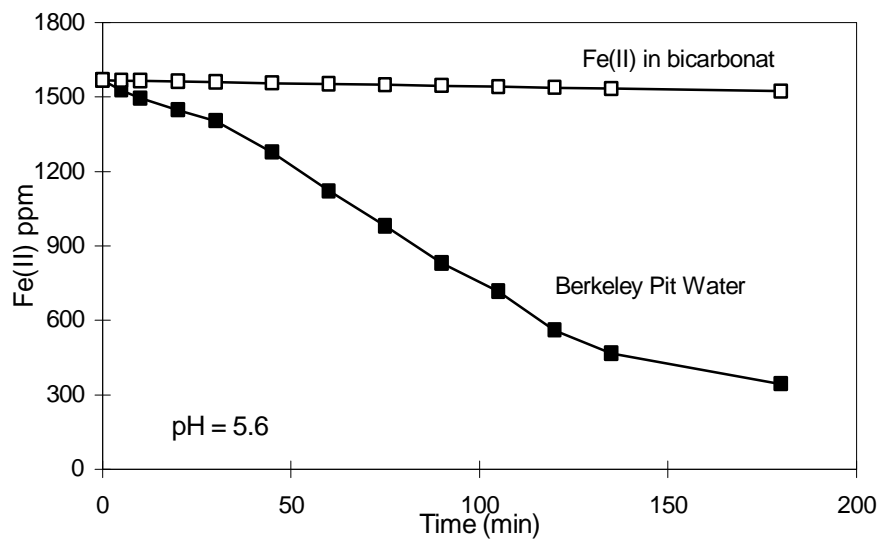


Figure 3-7. Fe(II) oxidation as a function of time in the Berkeley Pit compared to the bicarbonate system computed from the literature (Ref. 11). The initial Fe(II) concentration was 1,567 ppm.

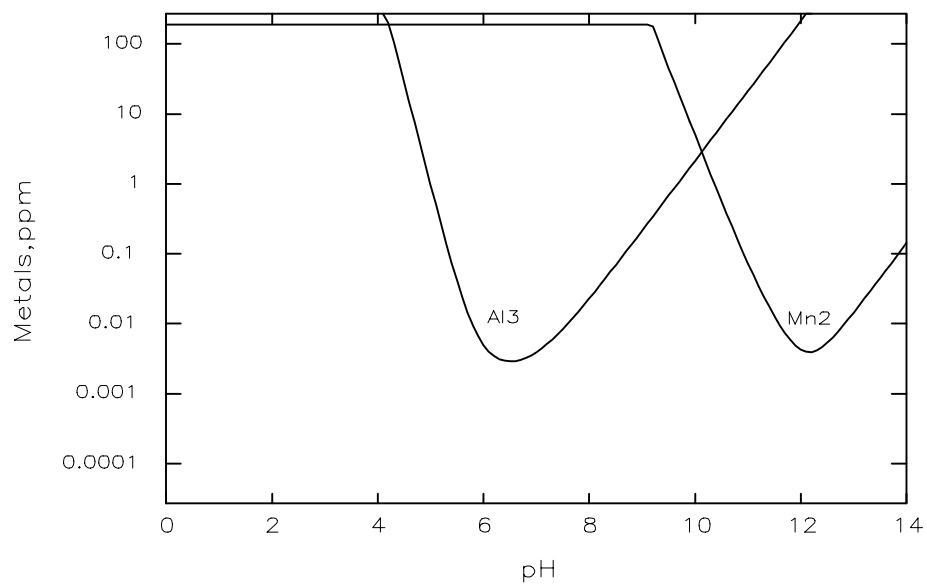


Figure 3-8. Calculated solubilities of Al and Mn versus pH in Berkeley Pit water (October 1992).

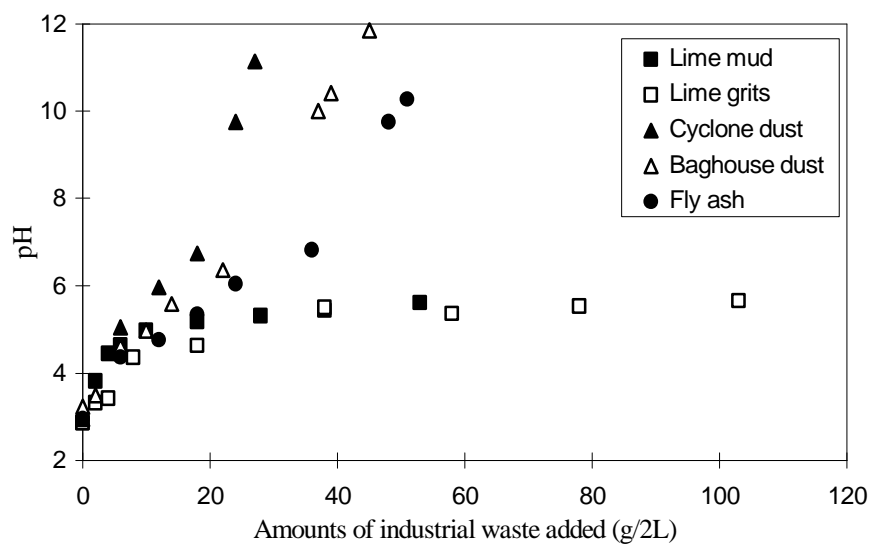


Figure 3-9. pH responses in Berkeley Pit water by adding industrial alkaline wastes.

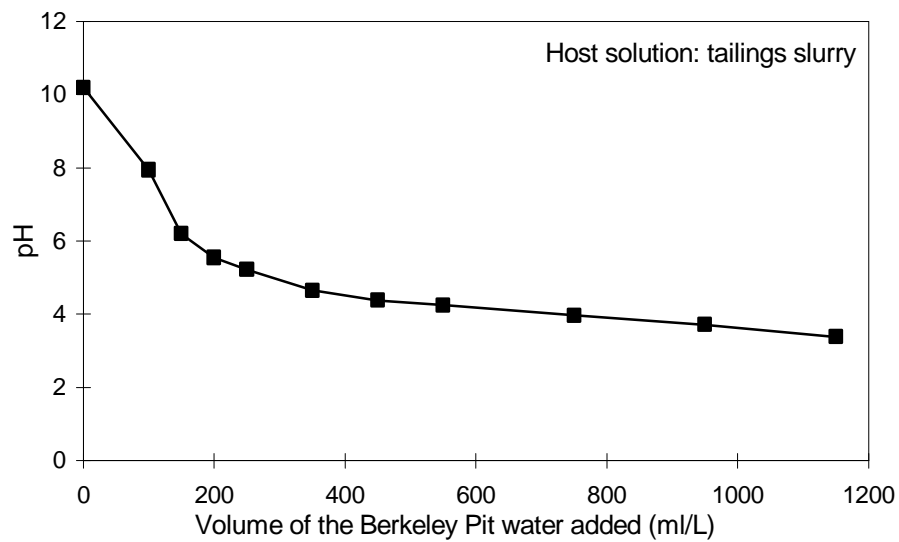


Figure 3-10. pH responses in the tailings slurry by adding Berkeley Pit water.

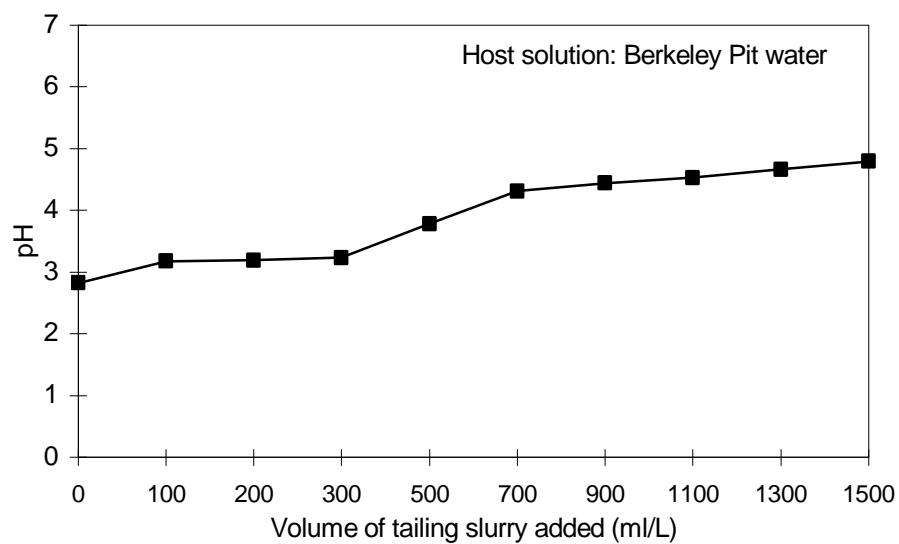


Figure 3-11. pH responses in Berkeley Pit water by adding the tailings slurry.
